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<p>(54) Title: FUEL ADDITIVE COMPOSITION</p> <p>(57) Abstract</p> <p>A homogeneous fuel additive composition which comprises: (a) a dispersant comprising a hydrocarbyl poly (oxyalkylene) aminocarbamate having at least one basic nitrogen atom and an average molecular weight of about 1000 to about 3000; (b) an injection detergent comprising a branched-chain hydrocarbyl amine having at least one basic nitrogen atom and an average molecular weight of about 300 to about 700, wherein the hydrocarbyl moiety is derived from polymers of C<sub>2</sub> to C<sub>6</sub> olefins; (c) a fuel demulsifier which is homogeneous with the other components of said fuel additive composition; and (d) a natural or synthetic carrier fluid.</p>			

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01

**FUEL ADDITIVE COMPOSITION**

02

03

**BACKGROUND OF THE INVENTION**

04

05 Numerous deposit-forming substances are inherent in  
06 hydrocarbon fuels. These substances when used in internal  
07 combustion engines tend to form deposits on and around  
08 constricted areas of the engine contacted by the fuel.  
09 Typical areas commonly and sometimes seriously burdened by  
10 the formation of deposits include carburetor air bleeds, the  
11 throttle body and venturies, engine intake valves and  
12 ports, fuel injection nozzles, cylinder head and piston top  
13 combustion chamber surfaces, etc.

14

15 Deposits adversely affect the operation of vehicles using  
16 hydrocarbon fuels. For example, deposits on the carburetor  
17 throttle body and venturies increase the fuel-to-air ratio  
18 of the gas mixture to the combustion chamber thereby  
19 increasing the amount of unburned hydrocarbon and carbon  
20 monoxide discharged from the chamber. High fuel-to-air  
21 ratios also reduce the gas mileage obtainable from the  
22 vehicle.

23

24 Deposits on the engine intake valves that are sufficiently  
25 heavy, restrict the gas mixture flow into the combustion  
26 chamber. This restriction starves the engine of air and  
27 fuel and results in a loss of power. Deposits on the valves  
28 also increase the probability of valve failure due to  
29 burning and improper valve seating. In addition, these  
30 deposits may break off and enter the combustion chamber  
31 possibly resulting in mechanical damage to the piston top,  
32 piston rings, cylinder head, etc.

33

34

01 It has long been known that the formation of these deposits  
02 can be inhibited as well as removed by incorporating an  
03 active detergent into the fuel. These detergents function  
04 to cleanse these deposit-prone areas of the harmful  
05 deposits, thereby enhancing engine performance and  
06 longevity.

07

08 The first generation of fuel additives consisted of  
09 detergents which helped to maintain the cleanliness of  
10 critical carburetor elements. These initial fuel additives  
11 were typically used in small doses, generally in the range  
12 of 15 to 30 ppm. Unfortunately, these small doses of  
13 additive provided little deposit control in other parts of  
14 combustion engines.

15

16 The next generation of fuel additives generally provided  
17 improved deposit control in the intake system including  
18 intake manifold hotspots, runners, intake valve ports, and  
19 intake valves. The extent of deposit control was typically  
20 modulated by controlling additive dose, usually in the range  
21 of 70 to 2,000 ppm. However, as additive doses increased to  
22 high levels, the accumulation of combustion chamber deposits  
23 became a significant problem for reasons which will become  
24 apparent hereinbelow.

25

26 In recent years the wide-spread use of non-leaded gasoline  
27 has further complicated the use of detergent-type gasoline  
28 additives. In automobile engines that require the use of  
29 non-leaded gasolines (to prevent disablement of catalytic  
30 converters used to reduce emissions), it has been found  
31 difficult to provide gasoline of sufficient octane to pre-  
32 vent knocking and the concomitant damage which it causes.  
33 The problem arises from an octane requirement increase,  
34

01 herein called "ORI", which results from deposits formed by  
02 the use of commercial gasolines.

03

04 The basis of the ORI problem is as follows: each engine,  
05 when new, requires a certain minimum octane fuel in order to  
06 operate satisfactorily without pinging and/or knocking,  
07 and/or after run. As the engine is operated on any  
08 gasoline, this minimum octane requirement increases. This  
09 is apparently caused by formation of deposits in the com-  
10 bustion chamber. In most cases, if the engine is operated  
11 on the same fuel for a prolonged period, the ORI will reach  
12 an equilibrium. Equilibrium is typically reached after  
13 5,000 to 15,000 miles of automobile operation.

14

15 The octane requirement increase in a particular engine used  
16 with commercial gasolines will vary at equilibrium from 4 to  
17 6 octane units to as high as 12 or 15 units, depending upon  
18 the gasoline compositions, engine design and type of oper-  
19 ation. The seriousness of the problem is thus apparent. A  
20 typical automobile with a research octane requirement of 85,  
21 when new, may after a few months of operation require 97  
22 research octane gasoline for proper operation, and little  
23 unleaded gasoline of that octane is available. The ORI  
24 problem also exists to some degree with engines operated on  
25 leaded fuels. U.S. Patent Nos. 3,144,311; 3,146,203; and  
26 4,247,301 disclose lead-containing fuel compositions having  
27 reduced ORI properties.

28

29 The ORI problem is compounded by the fact that the most  
30 common method for increasing the octane rating of unleaded  
31 gasoline is to increase its aromatic content. These aroma-  
32 tics, however, eventually cause an even greater increase in  
33 the octane requirement. Moreover, some of the nitrogen-  
34 containing compounds presently used as deposit-control

01 additives and their mineral oil or polymer carriers may also  
02 significantly contribute to ORI in engines using unleaded  
03 fuels.

04

05 It is, therefore, particularly desirable to provide deposit  
06 control additives at doses sufficient to effectively control  
07 the deposits in intake systems of engines without themselves  
08 significantly contributing to the ORI problem.

09

10 In this regard, the hydrocarbyl poly(oxyalkylene)  
11 aminocarbamate dispersants are commercially successful fuel  
12 additives which control induction system deposits without  
13 significantly contributing to the ORI problem. However,  
14 these additives are relatively expensive and this  
15 discourages their use in high concentrations.

16

17 At economical fuel concentrations, the hydrocarbyl  
18 poly(oxyalkylene) aminocarbamates are not quite as effective  
19 at controlling deposits in the injectors or carburetor of  
20 modern combustion engines. The performance of these  
21 engines, which contain fuel injection fuel delivery systems,  
22 can be substantially upset by relatively small amounts of  
23 deposits.

24

25 On the other hand, low molecular weight hydrocarbyl amine  
26 and polyamine detergents are known to effectively control  
27 deposits in injectors. These amine detergents are similar  
28 to those described earlier that were used to maintain clean  
29 carburetors. However, to control deposits on injectors,  
30 these detergents are used at fuel concentrations in the  
31 range of 40 to 70 ppm. It is now known that such high doses  
32 of injector detergents negatively impact the control of  
33 deposits on intake valves and in the combustion chamber of  
34 engines.

01 An additional problem with some low molecular weight  
02 hydrocarbyl amine and polyamine detergents that contain a  
03 primary or secondary amine functionality is the formation of  
04 a solid precipitate when the amine is exposed to carbon  
05 dioxide, such as exposure to the carbon dioxide in air. It  
06 is believed that this precipitate is a carbamic acid adduct  
07 formed by reaction of the primary or secondary amine with  
08 carbon dioxide. Whatever its chemical structure, formation  
09 of such a precipitate is undesirable for reasons which will  
10 be explained hereinbelow.

11

12 A further problem associated with some low molecular weight  
13 amines, particularly those containing polar substituents  
14 such as hydroxy groups, is the fact that these amines have a  
15 high water solubility, and therefore, on contact with water,  
16 can be completely extracted out of the hydrocarbon phase and  
17 into the water phase. As a result, such amines would have  
18 reduced effectiveness in hydrocarbon fuels.

19

20 In this regard, U.S. Patent No. 4,810,263 to Zimmerman et  
21 al. discloses an additive package for reducing and/or  
22 preventing fouling in a multiport fuel-injected engine which  
23 contains an amine oxide, such as bis(2-hydroxy ethyl)  
24 cocamine oxide, and a demulsifier comprising one or more  
25 demulsifying agents selected from a fatty acid alkylamine  
26 reaction product and a solution of oxyalkylated alkylphenol  
27 formaldehyde resins and polyglycols. U.S. Patent  
28 No. 4,836,829 to Zimmerman et al discloses a similar addi-  
29 tive package which contains a tertiary amine, such as  
30 bis(2-hydroxy ethyl) cocamine, preferably in combination  
31 with an amine oxide, and a demulsifying agent. As noted in  
32 U.S. Patent No. 4,810,263, the amine oxide typically has  
33 water present from the manufacturing process, which is  
34 difficult to completely remove. As a result, the amine

01 oxide is commercially available as an isopropyl alcohol  
02 solution which contains from 6 to 8 weight percent water.  
03  
04 Frequently, mineral oil carriers are used with either the  
05 amine detergents or the hydrocarbyl poly(oxyalkylene)  
06 aminocarbamate dispersants to assist in removing and  
07 preventing deposits. However, even with the addition of  
08 mineral oil carriers, neither group of fuel additives  
09 provides complete intake system deposit control.  
10  
11 It would, therefore, be particularly desirable to combine an  
12 intake valve and combustion chamber deposit control addi-  
13 tive, such as a hydrocarbyl poly(oxyalkylene) aminocarbamate  
14 dispersant, with an injector detergent, such as a low  
15 molecular weight amine or polyamine, and an effective amount  
16 of a carrier fluid to provide a multi-component, multi-  
17 functional fuel additive package which maximizes effective  
18 control of deposits throughout the entire intake system and  
19 combustion chamber of engines, and which itself does not  
20 significantly contribute to the octane requirement increase  
21 problem.  
22  
23 The choice of components for a multi-component,  
24 multi-functional deposit control fuel additive composition  
25 is not straightforward. The composition must provide  
26 effective deposit control at additive levels which are  
27 economical, and with additives which do not contribute to  
28 ORI. It is also essential that the composition remains  
29 homogeneous, i.e., a single liquid phase, under all field  
30 conditions, if the composition is to dependably deliver the  
31 expected deposit control performance when blended with fuel  
32 and in actual engine service.  
33  
34

01 In providing an effective fuel additive composition,  
02 maintaining a single liquid phase is critical. Typically,  
03 there are no practical means to re-homogenize an additive  
04 composition once distributed to the field. If the bulk  
05 additive composition separates into two or more phases, as a  
06 result of component incompatibility, neither phase will  
07 contain the effective combination of components intended for  
08 the fuel. Therefore, the overall deposit control per-  
09 formance of the fuel will be seriously degraded.  
10 Furthermore, the composition of additive delivered to the  
11 fuel will be erratic.

12

13 The phase separation of an incompatible composition can take  
14 many forms. Typically, the phase separation appears first  
15 as a haze which eventually settles out, either up or down,  
16 depending on the relative densities of the two phases. Thus  
17 as the level of additive in, for example, a storage tank is  
18 drawn down, the interface between the phases may pass below  
19 the liquid draw point, at which time the composition of  
20 additive flowing into the fuel will change, perhaps  
21 drastically.

22

23 A phase separation will also cause serious problems in the  
24 additive distribution system which distributes the additive  
25 composition to the fuel. If the phase separation involves  
26 two liquid phases, the heavier phase will collect on the  
27 bottom of the additive storage tank and at the low points of  
28 the additive delivery lines. This will result in the need  
29 for expensive and inconvenient periodic cleanout of the  
30 additive distribution equipment.

31

32 If the phase separation involves a solid separating from the  
33 bulk liquid additive composition, the effect would be more  
34 serious and immediate. Virtually all additive injection

01 systems have fine-mesh filters to protect the valves and  
02 seals in the injection pump. A solid phase would rapidly  
03 plug these filters and shut down the injector, thus  
04 requiring that the filter be cleaned before restarting the  
05 injector. A separate solid phase would also require the  
06 periodic cleaning of the additive storage tank. The  
07 criticality of a homogeneous additive composition is thus  
08 apparent.

09

10 It is generally considered beneficial to include a minor  
11 amount of a material which has fuel/water demulsifier  
12 properties in fuel blends of additive compositions. The  
13 demulsifier must exhibit demulsification properties when  
14 utilized in motor fuels at relatively low levels, such as 5  
15 to 25 parts per million. However, it has been observed that  
16 even low dosages of such material can, in certain instances,  
17 have a negative effect on the deposit-inhibiting properties  
18 of the additive composition. Consequently, it is desirable  
19 to choose a demulsifier which does not exhibit this negative  
20 effect. In addition, it is critical that the demulsifier  
21 remain homogeneous with the additive composition for reasons  
22 cited hereinabove.

23

24 It is also generally beneficial to include a solvent or  
25 diluent in the additive composition. The primary function  
26 of this component is to reduce the low-temperature viscosity  
27 of the composition. The solvent must however be compatible  
28 with the additive components and economical.

29

30 Relevant Art

31

32 U.S. Patent Nos. 4,160,648 and 4,191,537 disclose  
33 hydrocarbyl poly(oxyalkylene) aminocarbamates as fuel  
34 additives. The use of a fuel-soluble carrier oil and,

01 additionally, a demulsifier in combination with the  
02 hydrocarbyl poly(oxyalkylene) aminocarbamates is also  
03 disclosed.

04

05 The use of hydrocarbyl amines and hydrocarbyl polyamines as  
06 fuel additives is disclosed in U.S. Patent Nos.:

07

08 3,438,757; 3,898,056; and

09 3,565,804; 3,960,515

10 3,574,576

11

12 U.S. Patent Nos. 3,898,056 and 3,960,515 disclose a mixture  
13 of high and low molecular weight hydrocarbyl amines used as  
14 detergents and dispersants at low concentrations in fuels.

15 The high molecular weight hydrocarbyl amine contains at  
16 least one hydrocaryl group having a molecular weight from  
17 about 1,900 to 5,000 and the low molecular weight hydro-  
18 carbyl amine contains at least one hydrocarbyl group having  
19 a molecular weight from about 300 to 600. The weight ratio  
20 of low molecular weight amine to high molecular weight amine  
21 in the mixture is maintained between about 0.5:1 and 5:1.

22

23 While these references disclose hydrocarbyl poly(oxyalkylene)  
24 aminocarbamates useful as dispersants and hydrocarbyl amines  
25 and polyamines useful as detergents, none of these references  
26 teach a homogeneous additive composition comprising a dis-  
27 persant, detergent, carrier oil and demulsifier which, when  
28 mixed with fuel at low concentrations, provides effective  
29 deposit control throughout the entire intake system while  
30 minimizing contribution to the ORI problem.

31

32

33

34

01

SUMMARY OF THE INVENTION

02

03 The present invention provides a novel homogeneous fuel  
04 additive composition which comprises:

05

06 (a) a dispersant comprising a hydrocarbyl poly(oxyalkylene)  
07 aminocarbamate having at least one basic nitrogen atom  
08 and an average molecular weight of about 1,000 to about  
09 3,000;

10

11 (b) an injector detergent comprising a branched-chain  
12 hydrocarbyl amine having at least one basic nitrogen  
13 atom and an average molecular weight of about 300 to  
14 about 700, wherein the hydrocarbyl moiety is derived  
15 from polymers of C<sub>2</sub> to C<sub>6</sub> olefins;

16

17 (c) a fuel demulsifier which is homogeneous with the other  
18 components of said fuel additive composition; and

19

20 (d) a natural or synthetic carrier fluid.

21

22 The present invention further provides a fuel composition  
23 comprising a hydrocarbon boiling in the gasoline or diesel  
24 range and from about 400 to 1,200 parts per million of the  
25 homogeneous fuel additive composition described above.

26

27 The present invention is also concerned with a fuel  
28 concentrate comprising an inert stable oleophilic organic  
29 solvent boiling in the range of 150° to 400°F and from about  
30 5 to 50 weight percent of the homogeneous fuel additive  
31 composition of the invention.

32

33 Among other factors, the present invention is based on the  
34 surprising discovery that the unique combination of

01 dispersant, low molecular weight injector detergent,  
02 demulsifier and carrier fluid described herein provides com-  
03 plete intake deposit control while minimizing debilitating  
04 combustion chamber deposits, which correlate to ORI.

05

06 In addition, the use of a low molecular weight branched  
07 chain hydrocarbyl amine as an injector detergent avoids the  
08 precipitation problem associated with known amine deter-  
09 gents, such as oleyl amine.

10

11 DETAILED DESCRIPTION OF THE INVENTION

12

13 In essence, the present invention addresses the problem  
14 associated with the fact that none of the prior art fuel  
15 additives can singly, or in typical use concentration com-  
16 binations, provide complete gasoline intake system deposit  
17 control. The instant invention demonstrates a new formulat-  
18 ing technology which provides maximum deposit control in  
19 each critical deposit forming area while at the same time  
20 minimizing the doses of each critical ingredient. As a  
21 consequence, it is now possible to minimize the negative  
22 impact of each individual ingredient upon overall intake  
23 system and combustion chamber deposit control performance.

24

25 The instant invention describes a fuel additive composition  
26 which provides a homogeneous mixture of deposit control  
27 additives and carrier fluid, in individual proportions  
28 significantly below the levels historically recognized for  
29 maintaining adequate intake system deposit control in their  
30 respective areas of effectiveness, and an oil compatible  
31 demulsifier.

32

33

34

01 Accordingly, the novel fuel additive composition of the  
02 present invention is a homogeneous mixture which comprises  
03 the following components:

04

05 (a) a dispersant comprising a hydrocarbyl poly(oxyalkylene)  
06 aminocarbamate having at least one basic nitrogen atom  
07 and an average molecular weight of about 1,000 to about  
08 3,000;

09

10 (b) an injector detergent comprising a branched-chain  
11 hydrocarbyl amine having at least one basic nitrogen  
12 atom and an average molecular weight of about 300 to  
13 about 700, wherein the hydrocarbyl moiety is derived  
14 from polymers of C<sub>2</sub> to C<sub>6</sub> olefins;

15

16 (c) a fuel demulsifier which is homogeneous with the other  
17 components of said fuel additive composition; and

18

19 (d) a natural or synthetic carrier fluid.

20

21 In general, the homogeneous fuel additive composition of the  
22 invention will contain about 10 to 70 weight percent of the  
23 aminocarbamate dispersant, about 1 to 10 weight percent of  
24 the hydrocarbyl amine injector detergent, about 0.5 to  
25 5 weight percent of the fuel demulsifier and about 25 to  
26 80 weight percent of the carrier fluid. Although the  
27 present fuel additive composition can be used neat, it is  
28 often desirable to dilute the composition with an inert  
29 solvent or diluent, up to about 50 percent dilution.

30

31                   The Dispersant

32

33 The dispersant employed in the homogeneous fuel additive  
34 composition of the invention is a hydrocarbyl

01 poly(oxyalkylene) aminocarbamate having at least one basic  
02 nitrogen atom and an average molecular weight of about 1,000  
03 to 3,000. Thus the dispersant employed can be said to  
04 contain a poly(oxyalkylene) component, an amine component  
05 and a carbamate connecting group.

06

07 A. The Poly(oxyalkylene) Component

08

09 The hydrocarbyl-terminated poly(oxyalkylene) polymers  
10 which are utilized in preparing the carbamates of the  
11 present invention are monohydroxy compounds, e.g.,  
12 alcohols, often termed monohydroxy polyethers, or  
13 polyalkylene glycol monocarbyl ethers, or "capped"  
14 poly(oxyalkylene) glycals, and are to be distinguished  
15 from the poly(oxyalkylene) glycols (diols), or polyols,  
16 which are not hydrocarbyl-terminated, i.e., are not  
17 capped. The hydrocarbyl-terminated poly(oxyalkylene)  
18 alcohols are produced by the addition of lower alkylene  
19 oxides, such as oxirane, ethylene oxide, propylene  
20 oxide, butylene oxide, etc. to the hydroxy compound,  
21 ROH, under polymerization conditions, wherein R is the  
22 hydrocarbyl group which caps the poly(oxyalkylene)  
23 chain. In the poly(oxyalkylene) component employed in  
24 the present invention, the group R will generally  
25 contain from 1 to about 30 carbon atoms, preferably from  
26 2 to about 20 carbon atoms and is preferably aliphatic  
27 or aromatic, i.e., an alkyl or alkyl phenyl wherein the  
28 alkyl is a straight or branched-chain of from 1 to about  
29 24 carbon atoms. More preferably, R is alkylphenyl  
30 wherein the alkyl group is a branched-chain of 12 carbon  
31 atoms, derived from propylene tetramer, and commonly  
32 referred to as tetrapropenyl. The oxyalkylene units in  
33 the poly(oxyalkylene) component preferably contain from  
34 2 to about 5 carbon atoms but one or more units of a

01 larger carbon number may also be present. The  
02 poly(oxyalkylene) component employed in the present  
03 invention is more fully described and exemplified in  
04 U.S. Patent No. 4,191,537, the disclosure of which is  
05 incorporated herein by reference.

06

07 Although the hydrocarbyl group on the hydrocarbyl  
08 poly(oxyalkylene) component will preferably contain from  
09 1 to about 30 carbon atoms, longer hydrocarbyl groups,  
10 particularly longer chain alkyl phenyl groups, may also  
11 be employed.

12

13 For example, alkylphenyl poly(oxyalkylene)  
14 aminocarbamates wherein the alkyl group contains at  
15 least 40 carbon atoms, as described in U.S. Patent  
16 No. 4,881,945 to Buckley, are also contemplated for use  
17 in the present invention. The alkyl phenyl group on the  
18 aminocarbamates of U.S. Patent No. 4,881,945 will pre-  
19 ferably contain an alkyl group of 50 to 200 carbon  
20 atoms, and more preferably, an alkyl group of 60 to 100  
21 carbon atoms. The disclosure of U.S. Patent  
22 No. 4,881,945 is incorporated herein by reference.

23

24 **B. The Amine Component**

25

26 The amine moiety of the hydrocarbyl-terminated  
27 poly(oxyalkylene) aminocarbamate is preferably derived  
28 from a polyamine having from 2 to about 12 amine  
29 nitrogen atoms and from 2 to about 40 carbon atoms. The  
30 polyamine is preferably reacted with a hydrocarbyl poly-  
31 (oxyalkylene) chloroformate to produce the hydrocarbyl  
32 poly(oxyalkylene) aminocarbamate fuel additive finding  
33 use within the scope of the present invention. The  
34 chloroformate is itself derived from hydrocarbyl

01 poly(oxyalkylene) alcohol by reaction with phosgene.  
02 The polyamine, encompassing diamines, provides the  
03 product poly(oxyalkylene) aminocarbamate with, on the  
04 average, at least about one basic nitrogen atom per  
05 carbamate molecule, i.e., a nitrogen atom titratable by  
06 strong acid. The polyamine preferably has a carbon-to-  
07 nitrogen ratio of from about 1:1 to about 10:1. The  
08 polyamine may be substituted with substituents selected  
09 from hydrogen, hydrocarbyl groups of from 1 to about 10  
10 carbon atoms, acyl groups of from 2 to about 10 carbon  
11 atoms, and monoketone, monohydroxy, mononitro, mono-  
12 cyano, alkyl and alkoxy derivatives of hydrocarbyl  
13 groups of from 1 to 10 carbon atoms. It is preferred  
14 that at least one of the basic nitrogen atoms of the  
15 polyamine is a primary or secondary amino nitrogen. The  
16 polyamine component employed in the present invention  
17 has been described and exemplified more fully in U.S.  
18 Patent No. 4,191,537.

19

20 Hydrocarbyl, as used in describing the hydrocarbyl  
21 poly(oxyalkylene) and amine components used in this  
22 invention, denotes an organic radical composed of carbon  
23 and hydrogen which may be aliphatic, alicyclic, aromatic  
24 or combinations thereof, e.g., aralkyl. Preferably, the  
25 hydrocarbyl group will be relatively free of aliphatic  
26 unsaturation, i.e., ethylenic and acetylenic, particu-  
27 larly acetylenic unsaturation. The more preferred poly-  
28 amine finding use within the scope of the present inven-  
29 tion is a polyalkylene polyamine, including alkylene-  
30 diamine, and including substituted polyamines, e.g.,  
31 alkyl and hydroxyalkyl-substituted polyalkylene poly-  
32 amine. Preferably, the alkylene group contains from 2  
33 to 6 carbon atoms, there being preferably from 2 to 3  
34 carbon atoms between the nitrogen atoms. Examples of

01 such polyamines include ethylenediamine, diethylene tri-  
02 amine, triethylene tetramine, di(trimethylene) triamine,  
03 dipropylene triamine, tetraethylene pentamine, etc.  
04 Among the polyalkylene polyamines, polyethylene poly-  
05 amine and polypropylene polyamine containing 2-12 amine  
06 nitrogen atoms and 2-24 carbon atoms are especially pre-  
07 ferred and in particular, the lower polyalkylene poly-  
08 amines, e.g., ethylenediamine, diethylene triamine,  
09 propylene diamine, dipropylene triamine, etc., are most  
10 preferred.

11

12 C. The Aminocarbamate

13

14 The poly(oxyalkylene) aminocarbamate fuel additive used  
15 in compositions of the present invention is obtained by  
16 linking the amine component and the poly(oxyalkylene)  
17 component together through a carbamate linkage, i.e.,  
18



22 wherein the oxygen may be regarded as the terminal  
23 hydroxyl oxygen of the poly(oxyalkylene) alcohol  
24 component, and the carbonyl group -C(O)-, is preferably  
25 provided by a coupling agent, e.g., phosgene. In the  
26 preferred method of preparation, the hydrocarbyl  
27 poly(oxyalkylene) alcohol is reacted with phosgene to  
28 produce a chloroformate and the chloroformate is reacted  
29 with the polyamine. The carbamate linkages are formed  
30 as the poly(oxyalkylene) chains are bound to the  
31 nitrogen of the polyamine through the oxycarbonyl group  
32 of the chloroformate. Since there may be more than one  
33 nitrogen atom of the polyamine which is capable of  
34 reacting with the chloroformate, the aminocarbamate  
contains at least one hydrocarbyl poly(oxyalkylene)

01 polymer chain bonded through an oxycarbonyl group to a  
02 nitrogen atom of the polyamine, but the carbonate may  
03 contain from 1 to 2 or more such chains. It is pre-  
04 ferred that the hydrocarbyl poly(oxyalkylene) amino-  
05 carbamate product contains on the average, about 1  
06 poly(oxyalkylene) chain per molecule (i.e., is a  
07 monocarbamate), although it is understood that this  
08 reaction route may lead to mixtures containing  
09 appreciable amounts of di or higher poly(oxyalkylene)  
10 chain substitution on a polyamine containing several  
11 reactive nitrogen atoms. A particularly preferred  
12 aminocarbamate is alkylphenyl poly(oxybutylene) amino-  
13 carbamate, wherein the amine moiety is derived from  
14 ethylene diamine or diethylene triamine. Synthetic  
15 methods to avoid higher degrees of substitution, methods  
16 of preparation, and other characteristics of the amino-  
17 carbamates used in the present invention are more fully  
18 described and exemplified in U.S. Patent No. 4,191,537.

19

20 The Injector Detergent

21

22 The injector detergent employed in the homogeneous fuel  
23 additive composition of the present invention is a  
24 branched-chain hydrocarbyl amine having at least one basic  
25 nitrogen atom and an average molecular weight of about 300  
26 to about 700, and wherein the hydrocarbyl moiety is derived  
27 from polymers of C<sub>2</sub> to C<sub>6</sub> olefins.

28

29 In the amine injector detergent, the branched-chain  
30 hydrocarbyl group will ordinarily be prepared by polymer-  
31 izing olefins of from 2 to 6 carbon atoms (ethylene being  
32 copolymerized with another olefin so as to provide a  
33 branched-chain). The branched chain hydrocarbyl group will  
34 generally have at least 1 branch per 6 carbon atoms along

01 the chain, preferably at least 1 branch per 4 carbon atoms  
02 along the chain and, more preferably, at least 1 branch per  
03 2 carbon atoms along the chain. The preferred branched-  
04 chain hydrocarbyl groups are polypropylene and polyiso-  
05 butylene. The branches will usually be of from 1 to 2  
06 carbon atoms, preferably 1 carbon atom, that is, methyl. In  
07 general, the branched-chain hydrocarbyl group will contain  
08 from about 20 to 40 carbon atoms.

09

10 In most instances, the branched-chain hydrocarbyl amines are  
11 not a pure single product, but rather a mixture of compounds  
12 having an average molecular weight. Usually, the range of  
13 molecular weights will be relatively narrow and peaked near  
14 the indicated molecular weight.

15

16 The amino component of the branched-chain hydrocarbyl amines  
17 may be either a monoamine or a polyamine. The monoamine or  
18 polyamine component embodies a broad class of amines having  
19 from 1 to 10 amine nitrogen atoms and from 2 to 40 carbon  
20 atoms with a carbon to nitrogen ratio between about 1:1 and  
21 10:1. In most instances, the amine component is not a pure  
22 single product, but rather a mixture of compounds having a  
23 major quantity of the designated amine. For the more  
24 complicated polyamines, the compositions will be a mixture  
25 of amines having as the major product the compound indicated  
26 and having minor amounts of analogous compounds.

27

28 When the amine component is a polyamine, it will preferably  
29 be a polyalkylene polyamine, including alkylenediamine.  
30 Preferably, the alkylene group will contain from 2 to 6  
31 carbon atoms, more preferably from 2 to 3 carbon atoms.  
32 Examples of such polyamines include ethylene diamine,  
33 diethylene triamine, triethylene tetramine and tetraethylene  
34 pentamine.

01 A particularly preferred branched-chain hydrocarbyl amine is  
02 polyisobutetyl ethylène diamine.  
03  
04 The branched-chain hydrocarbyl amine injector detergents  
05 employed in the fuel additive composition of the invention  
06 are prepared by conventional procedures known in the art.  
07 Such branched-chain hydrocarbyl amines and their prepa-  
08 rations are described in detail in U.S. Patent  
09 Nos. 3,438,757; 3,565,804; 3,574,576; 3,848,056 and  
10 3,960,515, the disclosures of which are incorporated herein  
11 by reference.

12

13                   The Demulsifier

14

15 The demulsifier employed in the fuel additive composition of  
16 the invention is a chemical agent which, when used in  
17 relatively low concentrations in gasoline compositions, will  
18 promote the rapid coalescence of emulsified water to the  
19 point where it can be effectively removed from the bulk  
20 hydrocarbon by means of static gravity assisted separation  
21 in a quiescent storage tank. The demulsifier agent is  
22 frequently a mixture of several chemical agents which in  
23 proper combination afford the desired demulsifying charac-  
24 teristics. These agents are typically selected from, but  
25 are not restricted to, alkylphenol resins, polyoxyalkylene-  
26 based fluids, alkylarylsulfonates, derivatives of fatty  
27 acids, and the like. One preferred demulsifier for use in  
28 the composition of this invention is known as Tolad® T-326,  
29 a commercially available demulsifier from Petrolite  
30 Corporation, Tretolite Division, St. Louis, Missouri, which  
31 comprises a mixture of oxyalkylated alkylphenol-formaldehyde  
32 resins, polyoxyalkylene glycols, and sodium arylsulfonate in  
33 heavy aromatic naphtha.

34

20

01 In selecting a proper fuel/water demulsifying agent, it is  
02 important that the fuel, blended with an effective deposit  
03 control amount of a fuel additive, be able to shed water or  
04 become essentially emulsion-free within 15 to 30 minutes of  
05 its contact with an aqueous phase. The fuel additive com-  
06 position of this invention, being generally regarded as a  
07 dispersant agent, also has the tendency to promote emulsion  
08 formation when gasoline compositions containing the additive  
09 composition are contacted with water. Demulsifiers, at  
10 relatively low fuel concentrations, assist in the demulsifi-  
11 cation of such emulsions and thereby help to clarify other-  
12 wise cloudy wet fuels. It is important to note that  
13 demulsifiers, when used in concentrations higher than about  
14 25 ppm, can also promote emulsification. Hence, their  
15 dosage must be carefully regulated and adjusted to the  
16 physical/chemical characteristics of fuel compositions  
17 containing the fuel additive components. Many demulsifiers  
18 will satisfy this criterion but will nevertheless fail the  
19 criterion of compatibility with the other components of the  
20 fuel additive composition.

21

#### The Carrier Fluid

23

24 The carrier fluid employed in this invention is a chemically  
25 inert hydrocarbon-soluble liquid vehicle which substantially  
26 increases the nonvolatile residue (NVR), or solvent-free  
27 liquid fraction of the fuel additive composition while not  
28 overwhelmingly contributing to octane requirement increase.  
29 The carrier fluid may be a natural or synthetic oil, such as  
30 mineral oil, refined petroleum oils, synthetic polyalkanes  
31 and alkenes, synthetic polyoxyalkylene derived oils, and the  
32 like, as described, for example, in U.S. Patent  
33 No. 4,191,537 to Lewis. These carrier fluids are believed  
34

01 to act as a carrier for the dispersant and detergent and to  
02 assist in removing and retarding deposits.

03

04 The carrier fluid employed in the instant invention must  
05 also be capable of forming a homogeneous mixture with the  
06 other components of the present fuel additive composition.

07 Examples of suitable carrier fluids include Chevron Neutral  
08 Oil 500R and Chevron Neutral Oil 600P, available from  
09 Chevron U.S.A. Inc., San Francisco, California.

10

11 Fuel Compositions

12

13 The fuel additive composition of the present invention will  
14 generally be employed in a hydrocarbon distillate fuel  
15 boiling in the gasoline or diesel range. The proper concen-  
16 tration of this additive composition necessary in order to  
17 achieve the desired detergency and dispersancy varies  
18 depending upon the type of fuel employed, the presence of  
19 other additives, and the like. In general, however, from  
20 about 400 to 1,200 parts per million (ppm) of the instant  
21 fuel additive composition in the base fuel is needed to  
22 achieve the best results. In terms of individual compo-  
23 nents, fuel compositions containing the homogeneous fuel  
24 additive composition of the invention will generally contain  
25 about 100 to 225 ppm of the aminocarbamate dispersant, about  
26 10 to 70 ppm of the hydrocarbyl amine injector detergent,  
27 about 5 to 25 ppm of the demulsifier and about 250 to  
28 800 ppm of the carrier fluid.

29

30 The deposit control fuel additive composition of the present  
31 invention may also be formulated as a concentrate, using an  
32 inert, stable oleophilic organic solvent boiling in the  
33 range of about 150° to 400°F. Preferably, an aliphatic or an  
34 aromatic hydrocarbon solvent is used, such as benzene,

22

01 toluene, xylenes, or higher-boiling aromatics or aromatic  
02 thinners. Aliphatic alcohols of about 3 to 8 carbon atoms,  
03 such as isopropanol, isobutylcarbinol, n-butanol, and the  
04 like, in combination with hydrocarbon solvents are also  
05 suitable for use with the additive composition of the  
06 invention. In the fuel concentrate, the amount of the  
07 instant additive composition will be ordinarily at least 5  
08 percent by weight and generally not exceed 50 percent by  
09 weight, preferably from 10 to 30 weight percent.

10

11 In gasoline fuels, other fuel additives may also be included  
12 such as antiknock agents, e.g., methylcyclopentadienyl  
13 manganese tricarbonyl, tetramethyl or tetraethyl lead, tert-  
14 butyl methyl peroxide and various oxygenates, such as  
15 methanol, ethanol and methyl t-butyl ether. Also included  
16 may be lead scavengers such as aryl halides, e.g., dichloro-  
17 benzene or alkyl halides, e.g., ethylene dibromide. Addi-  
18 tionally, antioxidants and metal deactivators may be  
19 present.

20

21 In diesel fuels, other well-known additives can be employed  
22 such as pour point depressants, flow improvers, cetane  
23 improvers, etc.

24

25 The following examples are offered to specifically  
26 illustrate this invention. These examples and illustrations  
27 are not to be construed in any way as limiting the scope of  
28 this invention.

29

30

31

32

33

34

01

EXAMPLES

02

03

EXAMPLE 1

04

05

Preparation of an Aminocarbamate Dispersant  
Useful in this Invention

06

07

A dispersant useful in this invention was prepared in a manner similar to that described in Lewis, U.S. Patent No. 4,160,648, Examples 6-8, except that diethylene triamine was used in place of ethylene diamine. In this example, a tetrapropenyl phenol was reacted stepwise with butylene oxide, phosgene, and diethylene triamine to afford a high molecular weight tetrapropenyl poly(oxybutylene) aminocarbamate, referred to hereinbelow as a polyether amine (PEA).

16

17

EXAMPLE 2

18

19

A Hydrocarbyl Amine Injector  
Detergent Useful in this Invention

21

22

An injector detergent (ID) was prepared in a manner similar to that described by Honnen, U.S. Patent No. 3,438,757, Example 2. In this example, a C<sub>30</sub> polyisobutene having a molecular weight of approximately 420 was reacted stepwise with chlorine and ethylene diamine to produce a polyisobutene ethylene diamine adduct.

27

28

EXAMPLE 3

29

30

Carrier Fluids Useful in this Invention

32

33

34

Chevron Neutral Oil 500R and Chevron Neutral Oil 600P were used as carrier fluids (CF) in the examples hereinbelow. Chevron Neutral Oil 500R is a highly refined base oil having

24

01 a pour point of -12°C (Max.) and a viscosity of 98.6 cSt at  
02 40°C. Chevron Neutral Oil 600P is a highly refined base oil  
03 having a pour point of 10°F (-12.2°C) and a viscosity of  
04 129.5 cSt at 37.8°C.

05

06 EXAMPLE 4

07

08 A Demulsifier Useful in this Invention

09

10 The demulsifier (D) used in these examples to illustrate the  
11 present invention was a commercially available demulsifier  
12 (from Petrolite Corporation, Tretolite Division, St. Louis,  
13 MO) identified by the manufacturer as Tolad® T-326. This  
14 demulsifier comprises a mixture of oxyalkylated alkylphenol-  
15 formaldehyde resins, polyoxyalkylene glycols, and sodium  
16 arylsulfonate (1 to 5 weight percent) in heavy aromatic  
17 naphtha (30 to 60 weight percent). Tolad® T-326 is  
18 reported to have a flash point, SFCC, of 114°F, a pour  
19 point, ASTM D-97, of 5°F, and a viscosity of 263 SUS at  
20 60°F.

21

22 EXAMPLE 5

23

24 Demulsibility Test

25

26 The procedure described by ASTM Method D-1094 was used to  
27 test demulsibility. Here, the fuel phase and the interface  
28 are rated for clarity and for persistence of an interfacial  
29 emulsion layer. The fuel additive compositions were tested  
30 and rated numerically, on a scale from one to four. The  
31 number "one" was the highest rating for clarity, and "one"  
32 was the highest rating for persistence of an interfacial  
33 emulsion layer.

34

25

01 The fuel additive composition of this invention, exemplified  
02 by Sample 6A below, met the requirement of a rating of one,  
03 on both these tests.

04

05 EXAMPLE 6

06

07 Preparation of Fuel Additive Compositions

08

09 Two fuel additive compositions were prepared. 150 parts of  
10 the polyether amine of Ex. 1, 25 parts of the injector  
11 detergent of Ex. 2, 12 parts of a demulsifier, 212 parts of  
12 Chevron Solvent 25, (which is a mixture of C-9 blending  
13 aromatics available from Chevron U.S.A., Inc., San Francisco,  
14 California) and 450 parts of Chevron Neutral Oil 500R  
15 (Ex. 3) were mixed at room temperature with stirring in a  
16 200 ml flask.

17

18 Sample 6A contained Tolad<sup>(B)</sup> T-326 (as described in Ex. 4) as  
19 the demulsifier. Sample 6B contained L-1562 as the demulsi-  
20 fier. L-1562 is a commercially available demulsifier pur-  
21 chased from Petrolite Corporation, St. Louis, MO. A third  
22 additive composition, Sample 6C, contained oleyl amine as  
23 the injector detergent, and is shown for comparison pur-  
24 poses. Oleyl amine is a low molecular weight straight chain  
25 C<sub>18</sub> primary amine.

26

27 EXAMPLE 7

28

29 Compatibility Test

30

31 The compatibility test used was a modification of the  
32 procedure described by ASTM Method D-2273, except that,  
33 since a significant amount of diluent solvent (Chevron  
34 Solvent 25, a mixture of C-9 blending aromatics) was already

26

01 present in these compositions, this test was performed with-  
02 out further dilution. The test was performed in two parts.  
03 In Part A, the samples prepared by the procedure of  
04 Example 6 were held at ambient or room temperature (about  
05 20-25°C) for 24 hours. Each sample was then visually  
06 inspected for a secondary phase. If a secondary phase was  
07 observed, the sample was centrifuged and the volume percent  
08 of the secondary phase determined. If no secondary phase  
09 was observed, Part B of this test was performed.

10  
11 In Part B, the samples were cooled to 0°F and held at this  
12 temperature for 24 hours. Each sample was then visually  
13 inspected for a secondary phase. If a secondary phase was  
14 observed, the sample was centrifuged and the volume percent  
15 of the secondary phase determined.

16  
17 The results are reported in terms of volume percent of  
18 secondary phase sediment after centrifuging, which was  
19 either a liquid, a solid or a combination. Levels of  
20 sediment (or secondary phase) that exceed 0.005 vol.% are  
21 considered unacceptable.

22  
23 The fuel additive composition of this invention (Sample 6A)  
24 does not have any measurable volume percent of a secondary  
25 phase under these test conditions. However, when L-1562 was  
26 used as the demulsifier (Sample 6B), or when oleyl amine was  
27 used as the injector detergent (Sample 6C), significant and  
28 unacceptable levels of a secondary phase were observed.

29

30

31

32

33

34

27

	<u>Fuel Additive Composition</u>	Vol. %	Secondary Phase
		Part A (20-25°C)	Part B (0°F)
01			
02			
03			
04	Sample 6A.: 150 parts PEA (Ex 1)	<0.005	<0.005
05	25 parts ID (Ex 2)		
06	450 parts CF (Ex 3, Chevron 500R)		
07	212 parts Chev. Sol. 25		
08	12 parts T-326		
09	Sample 6B.: 150 parts PEA (Ex 1) (Comparative)	0.75	-
10	25 parts ID (Ex 2)		
11	450 parts CF (Ex 3, Chevron 500R)		
12	212 parts Chev. Sol. 25		
13	12 parts L-1562		
14	Sample 6C.: 150 parts PEA (Ex 1) (Comparative)	<0.005	0.05
15	25 parts oleyl amine		
16	450 parts CF (Ex 3, Chevron 500R)		
17	212 parts Chev. Sol. 25		
18	12 parts T-326		

For Sample 6B, a liquid second phase was observed at ambient temperature showing the incompatibility of the demulsifier with the other components of the fuel additive composition.

Sample 6C, containing oleyl amine as an injector detergent, was centrifuged after cooling to 0°F and showed a small volume (0.05 vol.%) of an insoluble solid sediment. Thus it failed the criterion that sediment levels must not exceed 0.005 vol.%.

#### EXAMPLE 8

#### Intake Valve Deposit Test

An unleaded regular grade gasoline was additized with fuel additive packages of this invention such that the fuel contained the following ingredients:

01

02           8A: 150 ppm of PEA (Ex 1)  
03            25 ppm of ID (Ex 2)  
04            450 ppm of CF (Ex 3, Chevron 600P)  
05            12 ppm of D (T-326)

06

07           8B: 150 ppm of PEA (Ex 1)  
08            25 ppm of ID (Ex 2)  
09            450 ppm of CF (Ex 3, Chevron 500R)  
10            12 ppm of D (T-326)

11

12         The gasolines were tested for intake valve keep-clean  
13         effectiveness using a procedure which utilizes a 1981  
14         Pontiac 2.5-liter engine mounted upon an engine test stand,  
15         and run for 90 hrs. This test simulates a type of severe  
16         field test service characterized by light load driving  
17         conditions. The effectiveness of an additive package is  
18         determined by averaging the weights of accumulated intake  
19         valve deposits obtained by the end of test, and comparing  
20         these results with those obtained using identical test  
21         conditions and the unadditized fuel. A good fuel additive  
22         package capable of complete intake system keep-clean  
23         performance will typically reduce base gasoline intake valve  
24         deposits.

25

26         Using the above test conditions, the unadditized base fuel  
27         test produced, on average, 1,090 milligrams of deposits per  
28         intake valve. The same gasoline containing a fuel additive  
29         package of this invention using Chevron Neutral Oil 600P,  
30         Example 8A, gave on average 23 milligrams of deposits per  
31         intake valve. When the above comparison was made between  
32         base fuel and an additized fuel containing Chevron Neutral  
33         Oil 500R, Example 8B, we observed an average of 299 milli-  
34         grams of intake valve deposits. These results are  
35         summarized below:

36

37

	<u>Fuel Blend Containing:</u>	<u>Av. Deposit Wgts.</u>
01		
02		
03	No Additive (Base Case)	1090 mg
04	8A	23 mg
05	8B	299 mg
06		
07	In both 8A and 8B, the average deposit weight is well below	
08	the base case, showing the effectiveness of the fuel	
09	additive composition of the invention.	
10		

11                   EXAMPLE 9

12

13                   Octane Requirement Increase Test

14

15 This test measures the potential that any gasoline additives  
16 may have in upsetting the octane requirements of gasoline  
17 operated engines. Over time, due to the buildup of deposits  
18 in the combustion chamber, higher octane gasoline is  
19 required to minimize engine knock. Unadditized gasolines  
20 contribute a baseline level of deposits which typically  
21 require a fuel having an octane value four numbers higher  
22 than the initial fuel used to start the test in order to  
23 minimize the increasing engine knock condition. Gasoline  
24 additives contribute to this problem to different degrees,  
25 and the magnitude of this contribution can be measured by  
26 comparisons with engine tests using additized fuel. The  
27 difference of ORI observed between the tests is that addi-  
28 tional increment of increased octane number required to  
29 further minimize engine knock and is generally referred to  
30 as the octane requirement increase attributable to the  
31 gasoline additive package itself. This value is typically  
32 referred to as the "additive ORI number".

33

34

01 This procedure utilizes a 1975 Toyota 2.2-liter engine  
02 mounted on an engine stand and equipped with a control  
03 system to carefully regulate test conditions and engine  
04 operating cycles. The engine is first run for fifteen hours  
05 on a relatively clean-burning, additive-free alkylate fuel.  
06 At this time, the octane requirement is determined, and the  
07 fuel is switched to a mixture of 70% unleaded regular  
08 gasoline and 30% of FCC Heavy gasoline. The FCC Heavy  
09 component is employed to increase the rate of combustion  
10 chamber deposit accumulation during this phase of the test.  
11 After 110 hours of additional engine operation, the final  
12 octane requirement measurement is made.

13

14 When tested in this manner, the fuel additive package of  
15 this invention contributed one half of one octane number  
16 more than the octane requirement observed for the unaddi-  
17 tized fuel (Test 9A). This increase was significantly less  
18 than that observed for a commercial gasoline additive  
19 package consisting of a heavy polybutene amine made from a  
20 polybutene containing, on average, 100 carbons per molecule,  
21 and having an average molecular weight of about 1450, which  
22 is reacted stepwise with chlorine and ethylene diamine, and  
23 a large dose of carrier oil (Test 9B).

	<u>Fuel Containing:</u>	<u>ORI Number</u>	<u>Increase Over Base</u>
26	Base: No Additive	4.0	0
27	Test 9A: 150 ppm PEA (Ex 1)	4.5	0.5
28	25 ppm ID (Ex 2)		
29	600 ppm CF (Ex 3, Chevron 500R)		
30	12 ppm D (T-326) (Ex 4)		
32	Test 9B: 250 ppm Heavy Polybutene Amine	7.0	3.0
33	1000 ppm CF (Ex 3, Chevron 500R)		

## 01 WHAT IS CLAIMED IS:

02

03 1. A homogeneous fuel additive composition which  
04 comprises:

05

06 (a) a dispersant comprising a hydrocarbyl  
07 poly(oxyalkylene) aminocarbamate having at least  
08 one basic nitrogen atom and an average molecular  
09 weight of about 1000 to about 3000;

10

11 (b) an injection detergent comprising a branched-chain  
12 hydrocarbyl amine having at least one basic nitro-  
13 gen atom and an average molecular weight of about  
14 300 to about 700, wherein the hydrocarbyl moiety  
15 is derived from polymers of C<sub>2</sub> to C<sub>6</sub> olefins;

16

17 (c) a fuel demulsifier which is homogeneous with the  
18 other components of said fuel additive  
19 composition; and

20

21 (d) a natural or synthetic carrier fluid.

22

23 2. The fuel additive composition according to Claim 1,  
24 wherein the hydrocarbyl group in component (a) contains  
25 from 1 to about 30 carbon atoms.

26

27 3. The fuel additive composition according to Claim 1,  
28 wherein the hydrocarbyl group in component (a) is an  
29 alkylphenyl group.

30

31 4. The fuel additive composition according to Claim 3,  
32 wherein the alkyl moiety in the alkylphenyl group is  
33 tetrapropenyl.

34

- 01 5. The fuel additive composition according to Claim 1,  
02 wherein the amine moiety of the aminocarbamate is  
03 derived from a polyamine having from 2 to 12 amine  
04 nitrogen atoms and from 2 to 40 carbon atoms.  
05
- 06 6. The fuel additive composition according to Claim 5,  
07 wherein the polyamine is a polyalkylene polyamine  
08 having 2 to 12 amino nitrogen atoms and 2 to 24 carbon  
09 atoms.  
10
- 11 7. The fuel additive composition according to Claim 6,  
12 wherein the polyalkylene polyamine is selected from the  
13 group consisting of ethylene diamine, propylene  
14 diamine, diethylene triamine and dipropylene triamine.  
15
- 16 8. The fuel additive composition according to Claim 1,  
17 wherein the poly(oxyalkylene) moiety of component (a)  
18 is derived from C<sub>2</sub> to C<sub>5</sub> oxyalkylene units.  
19
- 20 9. The fuel additive composition according to Claim 1,  
21 wherein the hydrocarbyl poly(oxyalkylene) amino-  
22 carbamate of component (a) is an alkylphenyl poly-  
23 (oxybutylene)aminocarbamate, wherein the amine moiety  
24 is derived from ethylene diamine or diethylene  
25 triamine.  
26
- 27 10. The fuel additive composition according to Claim 1,  
28 wherein the branched-chain hydrocarbyl moiety of  
29 component (b) is polypropenyl or polyisobutenyl.  
30
- 31 11. The fuel additive composition according to Claim 1,  
32 wherein the amine group of the branched-chain hydro-  
33 carbyl amine of component (b) is selected from the  
34 group consisting of ethylene diamine, diethylene

01        triamine, triethylene tetramine and tetraethylene  
02        pentamine.

03

04      12. The fuel additive composition according to Claim 1,  
05        wherein the branched-chain hydrocarbyl amine of  
06        component (b) is a polyisobutetyl ethylene diamine.

07

08      13. The fuel additive composition according to Claim 1,  
09        wherein component (a) is an alkylphenyl poly(oxy-  
10        butylene)aminocarbamate, wherein the amine moiety is  
11        derived from ethylene diamine or diethylene triamine,  
12        and component (b) is a polyisobutetyl ethylene diamine.

13

14      14. A fuel composition comprising a hydrocarbon boiling in  
15        the gasoline or diesel range and from about 400 to  
16        about 1,200 parts per million of a homogeneous fuel  
17        additive composition comprising:  
18

19        (a) a dispersant comprising a hydrocarbyl  
20        poly(oxyalkylene) aminocarbamate having at least  
21        one basic nitrogen atom and an average molecular  
22        weight of about 1000 to about 3000;

23

24        (b) an injector detergent comprising a branched-chain  
25        hydrocarbyl amine having at least one basic  
26        nitrogen atom and an average molecular weight of  
27        about 300 to about 700, wherein the hydrocarbyl  
28        moiety is derived from polymers of C<sub>2</sub> to C<sub>6</sub>  
29        olefins;

30

31        (c) a fuel demulsifier which is homogeneous with the  
32        other components of said fuel additive composi-  
33        tion; and

34

01           (d) a natural or synthetic carrier fluid.

02

03   15. The fuel composition according to Claim 14, wherein  
04        said fuel composition contains about 100 to 225 ppm of  
05        the dispersant of component (a), about 10 to 70 ppm of  
06        the injector detergent of component (b), about 5 to  
07        25 ppm of the demulsifier of component (c) and about  
08        250 to 800 ppm of the carrier fluid of component (d).

09

10   16. A fuel concentrate comprising an inert stable  
11       oleophilic organic solvent boiling in the range of 150°  
12       to 400°F and from about 5 to 50 weight percent of a  
13       homogeneous fuel additive composition comprising:

14

15       (a) a dispersant comprising a hydrocarbyl  
16        poly(oxyalkylene) aminocarbamate having at least  
17        one basic nitrogen atom and an average molecular  
18        weight of about 1000 to 3000;

19

20       (b) an injector detergent comprising a branched-chain  
21        hydrocarbyl amine having at least one basic  
22        nitrogen atom and an average molecular weight of  
23        about 300 to 700, wherein the hydrocarbyl moiety  
24        is derived from polymers of C<sub>2</sub> to C<sub>6</sub> olefins;

25

26       (c) a fuel demulsifier which is homogeneous with the  
27        other components of said fuel additive  
28        composition; and

29

30       (d) a natural or synthetic carrier fluid.

31

32

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# INTERNATIONAL SEARCH REPORT

International Application No PCT/US91/00934

## I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all)

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC (5) C10L 1/22

U.S.CI.: 44/329, 335, 387, 432

## II. FIELDS SEARCHED

Classification System	Minimum Documentation Searched *	Classification Symbols
	Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched *	
U.S.	44/329, 335, 387, 432	

## III. DOCUMENTS CONSIDERED TO BE RELEVANT \*\*

Category *	Citation of Document, <sup>16</sup> with indication, where appropriate, of the relevant passages <sup>17</sup>	Relevant to Claim No. <sup>18</sup>
A	US, A, 3,898,056 (HONNEN) 05 MARCH 1975 Column 7 to column 9, lines 1-27.	1, and 10-16
Y	US, A, 3,960,515 (HONNEN) 01 June 1976 Column 3, lines 31-56, column 4, lines 20-26 and column 9, example 4).	1 and 10-16
A	US, A, 4,191,537 (LEWIS ET AL) 04 March 1980 Column 2, lines 37-52, column 7, lines 6 to col 8, lines 1-62 and column 10, lines 24-end).	1-9 and 13-16
Y	US, A, 4,197,409 (LILBURN) 08 April 1980 Column 7, lines 43 to column 9, lines 1-49	1-9, and 13-16
A	US, A, 4,247,301 (HONNEN) 27 January 1981 Column 2, lines 50-64 and column 8, lines 29-41	1 and 10-16
A	US, A, 4,270,930 (CAMPBELL ET AL) 02 June 1981 Column 3, lines 9 to column 4, lines 1-13.	1-9 and 13-16

\* Special categories of cited documents: <sup>16</sup>

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"Z" document member of the same patent family

## IV. CERTIFICATION

Date of the Actual Completion of the International Search <sup>19</sup>

26 APRIL 1991

Date of Mailing of this International Search Report <sup>20</sup>

11 JUN 1991

International Searching Authority <sup>21</sup>

ISA/US

Signature of Authorized Officer: NGOC-HO

INTERNATIONAL DIVISION

MARGARET B. MEDLEY *Margaret B. Medley*

## FURTHER INFORMATION CONTINUED FROM THE SECOND SHEET

Y	US, A, 4,274,837 (LILBURN) 23 June 1981 Column 7, line 44 to column 9, lines 49 and column 11, lines 24-59.	1-9 and 13-16
A	US, A, 4,288,612 (LEWIS ET AL) 08 September 1981 Column 6, line 51 to column 8, lines 1-4 and column 9, line 29 to column 10, lines 1-21	1-9 and 13-16
Y	US, A, 4,810,263 (LIMMERMAN ET AL) 07 March 1989 Column 4, lines 11-15 and 33-39	1 and 14-16
A	US, A, 4,877,416 (CAMPBELL) 31 October 1989 Column 2, lines 59 to column 3, lines 1-30	1-16

V.  OBSERVATIONS WHERE CERTAIN CLAIMS WERE FOUND UNEARABLE\*

This international search report has not been established in respect of certain claims under Article 17(2) (a) for the following reasons:

1.  Claim numbers ..... because they relate to subject matter not required to be searched by this Authority, namely:

2.  Claim numbers ..... because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3.  Claim numbers ..... because they are dependent claims not drafted in accordance with the second and third sentences of PCT Rule 6.4(a).

VI.  OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING\*

This International Searching Authority found multiple inventions in this international application as follows:

1.  As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims of the international application.

2.  As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims of the international application for which fees were paid, specifically claims:

3.  No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim numbers:

4.  As all searchable claims could be searched without effort justifying an additional fee, the International Searching Authority did not invite payment of any additional fee.

## Remark on Protest

- The additional search fees were accompanied by applicant's protest.
- No protest accompanied the payment of additional search fees.